Sequential Oxidative and Reductive Bleaching of Stained and Pigmented Wool in a Single Bath

ABSTRACT

A new process applicable to bleaching of both stained and pigmented wool combines a conventional bleaching process for pigmentation with a recently reported single-bath oxidative/reductive bleaching process. Conventionally, pigmented fibers in wool are selectively bleached by a three-step process: mordanting with ferrous ions, thorough and specific rinsing, and then bleaching with hydrogen peroxide. The process is dependent on selective retention of ferrous species on melanin pigmentation, but some nonselective retention of ferrous ions on wool following rinsing leads, upon subsequent treatment with hydrogen peroxide, to an undesirable light brown discoloration from ferric species. The recently reported single-bath bleaching process, which was developed for stained wool, converts the unspent hydrogen peroxide of the initial oxidative bleaching step to a reductive substance *in situ* by reaction with thiourea followed by an appropriate pH adjustment to 7–8. When this process is combined with the ferrous mordanting procedure, pigmented and stained fibers are bleached, and any discoloring ferric species formed within the wool as a result of hydrogen peroxide are reduced to ferrous ions. Ferrous ions have a much lower affinity for wool than ferric ions and may be washed away easily. Overall, much superior bleaching with less physical damage is achievable by the new process than with conventional single- or multi-bath processes.

The occurrence of dark fibers in wool often gives rise to annoying and expensive problems for manufacturers at all stages of wool processing. Extensive literature is available on the occurrence of dark fibers in white wool [8–10, 15], and we refer the reader to them for further information on the subject. The degree of contamination of white wool by colored fibers has a significant influence on its commercial value, especially when the wool is to be processed into light or pastel-colored articles. Manual removal of these fibers is an extremely work- and cost-intensive, eye-straining job. Visualization can be facilitated by a technique proposed by Chudleigh *et al.* [5], whereby colored fiber contaminants in wool top may be detected using balanced illumination. The individual fibers in a mass of white wool are essentially transparent, and their images can be partially suppressed by a suitable choice of illumination to increase the contrast of the colored fibers [5].

If the dark fiber content in white wool is above an acceptable level [17] for white or pastel end uses, then those dark fibers need to be cleaned up to improve the appearance and increase the value of the goods. Often the wool tops and sliver of yarn are not tested properly for dark fiber content, and hence these impurities are first seen as dark fibers interwoven into the fabric matrix or in the end product. In such cases, the dark fibers have to be removed manually with tweezers. A more convenient and economical alternative is a wet treatment, which is much more productive and in many cases also cheaper.

The color of dark fibers ranges from black through shades of brown to light yellow, and lightening black fibers requires more severe wet treatments than the lighter ones. Wet treatment conditions, however, should not be too severe to damage wool excessively at the expense of lightening a few black fibers. Therefore, any wet treatments should be selective for areas of high dark fiber content. There have been numerous publications on the bleaching of hair [19–21] and dark wool fibers [2–4, 7, 13, 14, 16, 18]. Laxer and Whewell [14] first realized that black-brown pigmented fibers absorb iron from ferrous sulfate solutions more rapidly and to a greater extent than white fibers, probably owing to the formation of a metal complex with the melanin of the pigment granules. Union between the iron and the fiber is reasonably firm, and this bound iron is a useful catalyst for promoting bleaching when the iron-containing fibers are immersed in solutions of hydrogen peroxide [14].

All known processes for bleaching pigmented dark fibers are based on the use of peroxy compounds [2]. Wolfram *et al.* [20] have studied the mechanism of hair bleaching in detail. They found that the bleaching reaction occurs in two steps: the initial solubilization of the granules is followed by the decolorization of the dark brown solubilized pigment. Wolfram *et al.* [20] showed that neither reducing agents such as thioglycolic acid, borohydride, sulfide, and sulfite nor some oxidizing agents such as persulfate, perchlorate, iodate, and permanganate produce any apparent physical change in the melanin pigment. Hydrogen peroxide displayed a different behavior. Dilute aqueous solutions of this reagent caused disintegration of the pigment granules, which slowly dissolved in the reaction system. The dark brown solution gradually became lighter over a long period of time. The second step (decolorization of the melanin granules) is therefore much slower than the first step (solubilization of the melanin pigment) and hence the former is the rate-determining step in the overall process. The disintegration process alone is unlikely to affect the color of hair significantly; it may cause only a slight change in hue.

The dissolution of melanin in alkali, observed for example in the "bleeding" of pigmented fibers even at only a slightly alkaline pH, is a well known phenomenon [13]. Bereck and Kaplin [3] have studied the disintegration of melanin granules in chemically treated karakul wool using an electron microscope. Their studies revealed the following interesting features: Under identical bleaching conditions, the destruction of the melanin granules was virtually complete in the mordanted wool, whereas in the untreated wool the granules were only partly dissolved. These workers have also observed that the electron micrographs of bleached wool were not unlike those of the samples treated with alkali. The change in luminosity due to the alkali treatment was negligible, however, compared with the relatively high luminosity of the bleached wool [3]. This strongly supports the view of Wolfram *et al.* [20] that melanin disintegration does not significantly influence fiber color. It may be said that the solubilized melanin stains the fibers in the same way as a black dyestuff [3]. A mixture of hydrogen peroxide and ammonium or potassium persulfate has been used successfully in the bleaching of melanin granules [6].

There had been extensive research on the selective bleaching of dark fibers using Bereck's iron mordanting technique [2], and the process was adopted successfully by many West German textile mills. This process consists of three stages—mordanting, rinsing, and bleaching. Bereck [2] particularly pointed out the importance of a proper choice of reducing agents in the application of ferrous salts to wool during mordanting and the thorough rinsing of the "loosely bound" ferrous and ferric ions from wool. He re-emphasized this in later work with others [4]. Of the many reducing agents tested, hypophosphorous and phosphorous acids proved to be the best stabilizing agents for minimizing damage to the wool fiber [2]. Giesen and Ziegler [11] have studied the absorption of iron by wool and hair, and they concluded from their studies that optimum conditions for selective absorption of iron by dark fibers in wool were achieved within a pH range of 3.0–3.5, using a treatment time of 60 minutes at 80°C. Within the pH range mentioned above, the pigmented karakul wool absorbed the greatest amount of iron. At higher pH values, the absorption of iron by pigmented karakul wool diminished as the maximum uptake of iron by nonpigmented merino wool was reached at pH 4.5 [11]. Here, it would be disadvantageous to work at pH values greater than 3.5 due to an increase in iron uptake by nonpigmented wool, which may cause extensive damage and discoloration during bleaching.

Provided the three stages of the process are done properly, an effective selective bleaching of the dark fibers with minimal damage is possible. Even though the three-step process may be carefully conducted, there always remains some residual trivalent iron, which tends to give an overall undesirable reddish-brown cast to the wool. Bereck *et al.* [4] already have shown that selective bleaching hardly alters the natural cream color of wool; such changes are also usually not desirable. However, increasing demand for "bleached white" material led Finnimore and Bereck [7] to investigate the further bleaching of selectively bleached material. Selectively bleached wool was given a second step reductive or oxidative bleaching to yield whiter material for customer requirements.

In this paper, we present an alternative approach to the bleaching of dark fibers in wool, where the oxidative bleach bath of the selective bleaching process is treated with thiourea to create a reductive bleaching medium *in situ* to further whiten wool in a single-bath operation. We discussed the reaction of thiourea with hydrogen peroxide under bleaching conditions in detail in a previous paper [1].

Experimental

The wool used was a flannel fabric (507 g/m^2) heavily contaminated with black hair and yellow-stained wool, kindly supplied by Forstmann and Co., Inc.,[2] Dublin, GA. The hydrogen peroxide used was a

[2] Reference to a particular brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

30% (w/w) aqueous solution. The nonionic wetting agent Triton X-100 was provided by Rohm and Haas Co., Philadelphia, PA. Tetrasodium pyrophosphate decahydrate was obtained from Aldrich Chemicals Co., Inc., Milwaukee, WI. All other chemicals used were of ACS grade.

BLEACHING TREATMENTS

The wool fabric was mordanted and bleached using an Ahiba Texomat (Ahiba Inc., Charlotte, NC) laboratory dyeing apparatus. Oxidation potential was monitored on a voltmeter using a Corning platinum redox combination electrode, a high quality platinum sensing element, and a sealed Ag/AgCl reference element (Fisher Scientific Co., Springfield, NJ); pH was monitored on an E & K pH meter (E & K Scientific Products, Saratoga, CA) using a combination glass electrode (Cole-Parmer International, Chicago, IL). All laboratory mordanting and bleaching trials were done at a liquor/wool ratio of 30:1.

Mordanting and Rinsing

Wool flannel fabric (10.0 g) was introduced into the mordant bath at 40°C, and the temperature was then raised to 80°C over a period of 20 minutes. Further mordanting was done at this temperature for 1 hour. The mordant solution consisted of $FeSO_4 \cdot 7H_2O$ (10.0 g/l), a reducing agent—hypophosphorous acid (0.2 g/l) or sodium bisulfite (2.0 g/l)—and Triton X-100 wetting agent (1.0 g/l); the initial pH was 2.87 and the pH after mordanting was 3.45.

After mordanting, the flannel was then removed and thoroughly rinsed four times in changes of deionized water at 80°C, each rinsing being for 5 minutes under acidic conditions (pH = 2.0–3.5). The flannel was then air dried.

Bleaching

Bleaching was done under alkaline conditions for a specified time and temperature in a bleach solution of hydrogen peroxide (30% w/w; 20.0 ml/l), tetrasodium pyrophosphate decahydrate (10.0 g/l), and Triton X-100 (1.0 g/l). The pH was maintained at 8.0–8.5 with aqueous ammonia; the initial pH was 9.37 prior to the addition of wool, and the pH after bleaching was 8.2–8.5.

WHITENESS AND YELLOWNESS INDICES AND ALKALI SOLUBILITY

Whiteness (ASTM, E-313) and yellowness (ASTM, D-1925) indices were measured with a Colorgard System 1000 tristimulus colorimeter (Pacific Scientific Co., Gardner Neotec Division, Silver Spring, MD). A quartz halogen lamp at a color temperature of 2854 K with 360° circumferential illumination (CIE Source C, 1931 standard observer illuminant) geometry was used at 45° from the sample's normal direction, sample viewing being at 0°. The equations used in the Colorgard System for calculating whiteness and yellowness indices are

$$WI = 3.387Z - 3Y$$

and

$$YI = [100(1.277X - 1.06Z)]/Y$$

where X, Y, and Z are the measured tristimulus values.

The extent of degradation of the wool caused by bleaching was determined by measuring the weight loss of the sample after immersion in 0.1 M sodium hydroxide for 1 hour at 65 ± 0.5°C [12].

Results and Discussion

Table I shows the effectiveness of the process of mordanting followed by rinsing and bleaching compared with conventional bleaching. First of all, the table reveals that the differences in whiteness and yellowness indices of the samples of treatments A and C are very small, even though we would have expected to obtain a whiter sample with the mordanted wool (treatment C). There are two possible explanations to account for this behavior. First, the samples used in the investigations are yellow-stained wool with substantial black hair content. Since we selected the conditions to yield optimum selective bleaching of black hair, we did not expect that the bleaching of the non-pigmented areas—the majority of the wool fibers—would be higher in one case than the other. The color indices are not expected to be sensitive to changes in the relatively few pigmented fibers. The human eye, however, is more discriminating: close examination reveals that the black hairs in the bleached mordanted wool have turned into a pale light brown shade that blends well with the background color of wool. The situation is quite different for the bleached non-mordanted wool: the black hairs have turned into a brown shade and are still readily detected by the eye. Second, ferrous ions, even if present in only a small amount after the rinsing step, may cause a red-brown discoloration to the overall appearance of wool as a result of the oxidation of ferrous species by hydrogen peroxide during the bleaching stage. This may well account for the small differences in the whiteness and yellowness indices of the mordanted versus nonmordanted bleached wool (treatment C versus A).

TABLE I. The effect of mordanting and the reducing agents used during mordanting on the efficiency of bleaching of dark fibers in wool flannel.

Treatment conditions	Whiteness index[a]	Yellowness index[b]	Alkali solubility, %[c]
Control (untreated)	−4.40 ± 0.30	32.70 ± 0.16	11.57 ± 0.30
A: H_2O_2[d]	15.09 ± 0.20	23.47 ± 0.07	21.50 ± 0.63
B: A, then thiourea[e]	19.33 ± 0.32	21.28 ± 0.11	18.21 ± 0.43
C: Fe^{2+}, H_3PO_2, then A[f]	14.47 ± 0.34	23.97 ± 0.13	22.24 ± 0.21
D: Fe^{2+}, H_3PO_2, then B[g]	19.49 ± 0.04	21.43 ± 0.03	20.13 ± 0.95
E: Fe^{2+}, $NaHSO_3$, then A[f]	21.73 ± 0.24	22.72 ± 0.01	26.95 ± 0.82
F: Fe^{2+}, $NaHSO_3$, then B[g]	26.14 ± 0.31	20.55 ± 0.12	23.11 ± 0.09

[a] As per ASTM E-313; mean value of 3 samples ± standard deviation, each sample having 8 measurements. [b] As per ASTM D-1925; mean value of 3 samples ± standard deviation, each sample having 8 measurements. [c] As per IWTO-4-60; mean value of 3 samples ± standard deviation. [d] Alkaline bleaching, 90 minutes, 60°C, as per Experimental (no mordanting). [e] As per treatment A for 60 minutes, followed by addition of thiourea (5.83 g/l), pH adjustment to 7–8, and bleaching for an additional 30 minutes. [f] Mordanting and rinsing as per Experimental followed by bleaching as per treatment A. [g] Mordanting and rinsing as per Experimental followed by bleaching as per treatment B.

We also investigated the effect of different reducing agents during mordanting on the bleaching efficiency of wool. In this study, we compared hypophosphorous acid to sodium bisulfite (Table I, treatments C and E, respectively). Both compounds were effective reducing agents in the application of ferrous ions onto wool and thus effective for selectively bleaching black hair. When the results of the bleaching trials are closely compared, it is easy to see that bleached wool mordanted in the presence of sodium bisulfite has a higher whiteness index and a lower yellowness index than the wool mordanted in the presence of hypophosphorous acid. This is because the wool mordanted in the presence of sodium bisulfite absorbed more iron (much darker color appearance after mordanting) than that mordanted in the presence of hypophosphorous acid. The excess iron will lead to a greater reaction of hydrogen peroxide and hence permit more efficient bleaching. We monitored hydrogen peroxide decomposition during bleaching in the presence of wool samples that had undergone different treatments; the results are shown in Figure 1. Here we see enhanced decomposition of hydrogen peroxide using wool that was mordanted in the presence of sodium bisulfite.

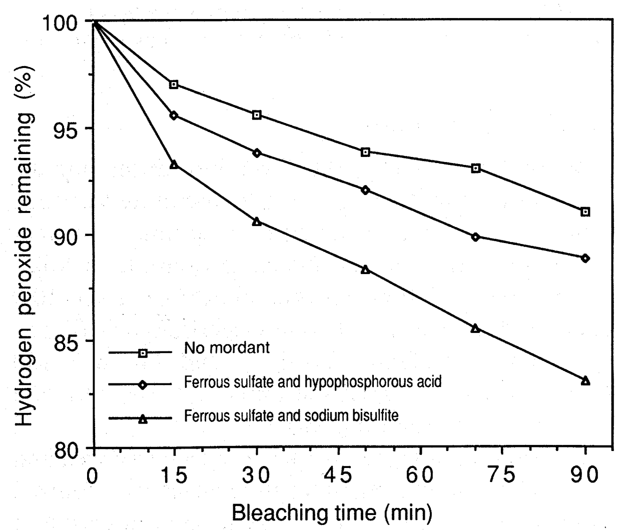

FIGURE 1. Decomposition of hydrogen peroxide in the bath during bleaching of wool. Conditions as per Table I as follows: "no mordant," treatment A; "ferrous sulfate with hypophosphorous acid," treatment C; "ferrous sulfate with sodium bisulfite," treatment E.

Absorption of excessive amounts of iron during mordanting and retention after thorough rinsing may cause excessive damage to wool during bleaching. This is reflected in the alkali solubility results presented in Table I. Note the higher alkali solubility in the case of iron and sodium bisulfite treated wool. Bereck [2] investigated numerous reducing agents for his process and concluded that hypophosphorous and phosphorous acids were the agents of choice. We infer from our data that bisulfite is not as good a reducing agent as hypophosphorous acid for stabilizing ferrous species on wool, that excessive amounts of ferric ion form on the wool (and are even visible as a reddish-brown discoloration), and that subsequent rinsing followed by treatment with hydrogen peroxide leads to excessive decomposition of peroxide and limited damage to the wool fiber despite good whiteness.

The results of the bleaching trials in combination with thiourea are also presented in Table I. We discussed thiourea-assisted bleaching in detail in the earlier work [1] and so will not report further on it here. The results in Table I clearly show that any of the bleaching trials mentioned above, when combined with thiourea and appropriate pH adjustment, yield much superior bleaching. This is very apparent when we compare treatments A and B, C and D, and E and F. The increase in whiteness index values and the decrease in yellowness index values are due to further bleaching of heavily yellow-stained wool and the substantial lightening of the background discoloration caused by ferric species.

We investigated the effect of various agents such as oxalic acid, sodium oxalate, and EDTA-disodium salt on the lightening of background discoloration on wool, and we present the results in Table II. We compared these results, in turn, with those of no aftertreatment and thiourea treatment. We thought at first that the agents mentioned above would chelate with and solubilize the iron present on wool after the bleaching stage and hence lighten the background discoloration. However, no after-treatments except thiourea gave any improvement in the lightening of wool as compared to the wool not given an after-treatment. The reaction of thiourea with the residual hydrogen peroxide after the bleaching stage and the necessary pH adjustment create a highly reductive agent that reduces any ferric species that may be present on wool to the ferrous form, which is easily washed away because of its much smaller affinity to white wool. Prolonged treatment with thiourea (25 minutes as compared to 5 minutes) yields a whiter, less yellow sample due to further bleaching of the heavily yellow-stained wool. The alkali solubilities in all cases are within acceptable limits.

Conclusions

We have developed a bleaching protocol that combines selective bleaching of pigmented fibers with oxidative/reductive bleaching of stained wool. Mordant bleaching using ferrous ion catalysis and hydrogen peroxide may be followed by *in-situ* generation of reductive bleach. The reductive system produces superior whiteness and prevents the deposition of ferric species and associated reddish stain from residual mordanting iron.

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Literature Cited

1. Arifoglu, M., Marmer, W. N., and Carr, C. M., Sequential Oxidative and Reductive Bleaching of Wool in a Single Bath, *Textile Res. J.* **60**, 319–328 (1990).
2. Bereck, A., Bleaching of Dark Fibres in Wool, in "Proc. 7th Int. Wool Res. Conf., Tokyo," vol. IV, 1985, pp. 152–162.
3. Bereck, A., and Kaplin, J. J., Electron-microscope Observations on the Disintegration of Melanin Granules in Chemically Treated Karakul Wool, *J. Textile Inst.* **74**, 44–47 (1983).
4. Bereck, A., Zahn, H., and Schwarz, S., Das Selective Bleichen von Pigmentierten Haaren in rohweisser Wolle, *Textil Prax. Int.* **37**, 621–629 (1982).
5. Chudleigh, P. W., Foulds, R. A., and Wong, P., Detecting Colored Fiber Contaminants in Wool Top Using Balanced Illumination, *Textile Res. J.* **55**, 233–238 (1985).
6. Corbett, J. F., The Chemistry of Hair-care Products, *J. Soc. Dyers Colour.* **92**, 285–303 (1976).
7. Finnimore, E., and Bereck, A., Verhalten von selectiv gebleichter Wolle, *Melliand Textilber.* **68**, 669–672 (Eng. trans., E291–292) (1987).
8. Fleet, M. R., Pigmented Fibres in White Wool, *Wool Technol. Sheep Breed.* **33**, 5–13 (1985).
9. Fleet, M. R., Stafford, J. E., Dawson, K. A., and Dolling, C. H. S., Contamination of White Wool by Melanin-pigmented Fibres when Pigmented and White Sheep Graze Together, *Aust. J. Exp. Agric.* **26**, 159–163 (1986).
10. Foulds, R. A., Wong, P., and Andrews, M. W., Dark Fibres and Their Economic Importance, *Wool Technol. Sheep Breed.* **32** (2), 91–100 (1984).

TABLE II. The effect of various aftertreatments on the optical properties of bleached wool flannel.[a]

Aftertreatment, conc., g/l	Whiteness index[b]	Yellowness index[c]	Alkali solubility[d]
None	20.89 ± 0.03	23.06 ± 0.13	20.65 ± 0.54
A: oxalic acid (3.0)	17.09 ± 0.84	24.99 ± 0.32	19.63 ± 1.36
B: sodium oxalate (3.0)	19.79 ± 0.24	23.60 ± 0.09	
C: EDTA, Na_2 salt (3.0)	19.34 ± 0.04	23.93 ± 0.07	
D: thiourea[e] (5.83)	25.47 ± 0.32	20.62 ± 0.18	
E: thiourea[ef] (5.83)	27.78 ± 0.59	19.70 ± 0.28	16.44 ± 0.25

[a] As per treatment C, Table I, but with total bleaching time and temperature adjusted to 65 minutes and 65°C. Aftertreatment is accomplished by direct addition to the bleaching bath of the appropriate reagent at 60 minutes. [b] As per Table I, footnote a. [c] As per Table I, footnote b. [d] As per Table I, footnote c. [e] With adjustment of pH to 7–8. [f] As per aftertreatment D, but with reagent added at 40 minutes.

11. Giesen, M., and Ziegler, K., Die Absorption von Eisen durch Wolle und Haar, *Melliand Textilber.* **62,** 482–483 (Eng. trans., E622–625) (1981).
12. IWTO Technical Committee Report, Method of Test for Solubility of Wool in Alkali, IWTO-4-60(E) 1960.
13. Kriel, W. J., Albertyn, D., and Swanepoel, O. A., Melanin-bleeding of Pigmented Karakul Wool, *S. Afr. Wool Textile Res. Inst. Bull.* **3** (1), 16–20 (1969).
14. Laxer, G., and Whewell, C. S., Some Physical and Chemical Properties of Pigmented Animal Fibres, in "Proc. Int. Wool Res. Conf. Australia," vol. F, 1955, pp. 186–200.
15. Nolan, C., and Foulds, R., Dark-fibre Contamination in Wool, *Queensl. Agric. J.* Nov.–Dec., 305–307 (1985).
16. Teasdale, D. C., and Bereck, A., The Measurement of the Color of Bleached and Natural Karakul Wool, *Textile Res. J.* **51,** 541–549 (1981).
17. Turner, T. R., and Foulds, R. A., Decision Schemes for Assessing Dark Fiber Concentration in Top, *Textile Res. J.* **57** (12), 710–720 (1987).
18. Van Heerden, N., Becker, J., van der Merwe, J. P., and Swanepoel, O. A., Bleaching of Karakul Wool, *S. Afr. Wool Textile Res. Inst. Bull.* **3** (4), 21–23 (1969).
19. Wolfram, L. J., and Albrecht, L., Chemical and Photobleaching of Brown and Red Hair, *J. Soc. Cosmet. Chem.* **82,** 179–191 (1987).
20. Wolfram, L. J., Hall, K., and Hui, I., The Mechanism of Hair Bleaching, *J. Soc. Cosmet. Chem.* **21,** 875–900 (1970).
21. Zahn, H., Hilterhaus, S., and Strussmann, A., Bleaching and Permanent Waving Aspects of Hair Research, *J. Soc. Cosmet. Chem.* **37,** 159–175 (1986).